ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND APPLICATIONS OF RECOVERABLE SOLID SUPPORTED LIGAND FOR ATRP

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ATRP İÇİN GERİ KAZANILABİLİR KATI LİGAND SENTEZİ VE UYGULAMALARI

YÜKSEK LİSANS TEZİ

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Eren Elik, a **M.Sc.** student of ITU **Institute of Science and Technology/ Graduate School of Istanbul Technical University** student ID 515111040, successfully defended the **thesis** entitled "**Synthesis and Applications of Recoverable Solid Supported Ligand for ATRP**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my parents,

FOREWORD

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Eren ELİK
Chemist

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ABBREVIATIONS

AIBN : Azobisisobutyronitrile
ATRP : Atom Transfer Radical Polymerization
BPO : Benzoyl peroxide
DCM : Dichloromethane
DO : 1,4-Dioxane
DVB : Divinylbenzene
EBrP : Ethyl-2-bromopropionate
FRP : Free-Radical Polymerization
FT-IR : Fourier Transform Infrared Spectroscopy
GC : Gas Chromatography
GMA : Glycidyl methacrylate
GPC : Gel Permeation Spectroscopy
HMTETA : Hexamethyltriethylenetetramine
k_{act} : Rate constant of activation
k_{deact} **or** k_d : Rate constant of deactivation
k_p^{app} : Apparent rate constant of polymerization
k_p : Rate constant of polymerization
k_t : Rate constant of termination
MA : Methyl acrylate
MMA : Methyl methacrylate
MWD : Molecular Weight Distribution
NMP : Nitroxide-Mediated Polymerization
NMR : Nuclear Magnetic Resonance
PE : Polyethylene
PEG : Polyethylene Glycol
PDI : Polydispersity Index
PMDETA : *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine
PMMA : Poly (methyl methacrylate)
PS : Polystyrene
PVP : Polyvinylpyrrolidone
RAFT : Reversible Addition-Fragmentation Chain Transfer
St : Styrene
SFRP : Stable Free-Radical Polymerization
TEDETA : *N*,*N*,*N*′,*N*′-Tetraethyldiethylenetriamine
THF : Tetrahydrofuran
X : Halide Atom
XL : Cross-linked poly(glycidyl methacrylate)-TEDETA
X-PGMA : Cross-linked poly(glycidyl methacrylate)

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SYNTHESIS AND APPLICATIONS OF RECOVERABLE SOLID SUPPORTED LIGAND FOR ATRP

SUMMARY

Living radical polymerization mediated by a metal halide complex, named atom transfer radical polymerization (ATRP), has made significant progress since it was first developed. The basis of this technique is the reversible transfer of a halogen atom from a monomeric or polymeric alkyl halide to a transition metal complex, forming an organic radical and a transition metal complex with a higher oxidation state. The equilibrium between the transition metal complex with a lower oxidation state higher oxidation state species is strongly shifted toward the lower oxidation complex; hence, the concentration of radicals is kept low, termination is reduced, and monomer addition is controlled. The catalyst–ligand complex in ATRP plays a key role to control the chain growth, polymerization rate, and polydispersity. Generally, copper-based catalysts are used for ATRP and the ligands for copper-based catalysts are usually bipyridine or multidentate amines. The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal, should also allow expansion of the coordination sphere, and should allow selective atom transfer without promoting other reactions. Homogeneous catalysts are preferred in performing kinetic and mechanistic studies of the polymerization. Additionally, they can produce polymers with low polydispersities. However, homogeneous ATRP catalysts are difficult to separate from their products.

The main challenge for atom transfer radical polymerization is to minimize the amount of residual catalyst in the resulting polymers. The residual catalyst deeply colors the product (e.g., deep green using copper bromide-aliphatic amine and deep brown using copper bromide-bipyridine). Despite the fact that the catalyst residue can be removed from the product by silica gel or resin or by precipitation, this post purification technique is not only expensive but also wastes catalyst. Different supported catalyst systems on insoluble particles (mostly silica gel and PS particles) have been developed to reduce the catalyst residue and to reuse the catalysts.

Environmentally and economically, chelating polymers have been developed to reduce, to remove, and to regain heavy metals in industrial wastewaters. Several scientists used these types of polymers (soluble or insoluble) in ATRP as a ligand. The most popular one amongst chelating resins contains nitrogen atoms that have high adsorption capability and most selectivity to transition metal ions by forming complex readily.

In this work, *N*,*N*,*N'*,*N'*-tetraethyldiethylenetriamine was covalently bonded to cross-linked poly(glycidyl methacrylate) obtained by suspension polymerization, named XL. This insoluble ligand was further used to mediate the ATRP of styrene. In order

to investigate this system, several reaction parameters was studied, as well as, demonstrating re-initiation, to produce block copolymers, and reuse of the catalyst (with and without regeneration) in subsequent reactions. Regeneration process was performed with either reducing agent or both reducing agent and fresh CuBr catalyst. In all situations, polymerization carried out and demonstrated first-order kinetics. Although controlled polymerization was observed with regards to molecular weight and polydispersity, low initiator efficiency was shown in comparison with homogenous medium. The molecular weights did not match the predicted values, and polydispersities were high ($1.8 < M_w/M_n < 2.5$) compare to homogenous ATRP but were quite lower than some literature values. However, reducing activity of catalyst complex as reusing was improved by regeneration contrast to without regeneration. The main reasons for reduced control might be the limited mobility of the supported catalyst and/or the steric hindrance and incompabilities between the immobilized catalyst and the polymer chain, or another reason might be possibly due to the oxidation of Cu(I) to Cu(II) in the solid ligand therefore those reasons cause less efficient halide atom transfer compared with homogenous ATRP. Besides, the great majority of metal was removed from polymerization solution and the color residue in the resulting product was almost eliminated according to qualitative observations. All in all, the new obtained insoluble ligand could be used as insoluble and recoverable support for ATRP of styrene.

ATRP İÇİN GERİ KAZANILABİLİR KATI DESTEKLİ LİGAND SENTEZİ VE UYGULAMALARI

ÖZET

Metal katalizörlü yaşayan radikal polimerizasyonu, daha çok bilinen adı ile atom transfer radikal polimerizasyonu (ATRP), değişik topolojilerde doğrusal polimerler ve kopolimerler elde etmek için kullanılan en etkin kontrollü / "yaşayan" polimerizasyon metodu haline gelmiştir. Bu tekniğin temeli monomerik ya da polimerik halojenur molekülünden metal kompleksine halojen atomu transferi yapılmasına dayanır. Bu transfer sırasında organik bir radikal ve yüksek oksidasyon seviyesinde geçiş metali kompleksi oluşturulur. Yüksek oksidasyon seviyesindeki metal ligand çifti ile düşük oksidasyon seviyesindeki metal ligand çiftinin reaksiyon dengesi düşük oksidasyon seviyesi yönündedir. Bundan dolayı, radikal konsantrasyonu hep düşük seviyede tutularak sonlanma reaksiyonları azaltılır ve monomerin polimerleşmesi kontrol altına alınır. Katalizör-ligand kompleksi ATRP de zincir büyümesi kontrolünde, polimerizasyon hızında ve molekül ağırlığı dağılımında anahtar rol oynamaktadır. Atom transfer radikal polimerizasyonu için genellikle bakır tabanlı katalizörler kullanılır ve bu katalizörler için bipiridin ve çok dişli aminler kullanılır. Ligandın polimerizasyondaki asıl görevi, geçiş metali tuzunu organik ortamda çözülebilir hale getirerek, uygun reaktivite ve metal merkez ile aktif uç, deaktif uç arasındaki halojen yer değişimini düzenlemektir. Ligand, geçiş metali ile kuvvetli bir şekilde kompleks oluşturmalı, ayrıca koordinasyon küresinin genişlemesine izin vermeli ve diğer reaksiyonlara teşvik etmeden seçici atom transferinin gerçekleşmesini sağlamalıdır. Kinetik ve mekanistik çalışmalarda genellikle homojen katalizörler tercih edilirler. Buna ek olarak, homojen katalizörler atom transfer radikal polimerizasyonu reaksiyonlarında düşük molekül ağırlığı dağılımı (polidispersite indeksi) veren, genellikle 1'e yakın, polimerler sentezlenmesinde önemli rol oynarlar. Ancak, bu tip homojen katalizörleri atom transfer radikal polimerizasyonu sonucu oluşan polimerlerden ayırmak oldukça zordur. Bu katalizörler, genel olarak katalizör kalıntıları şeklinde polimerle beraber çökelirler. Bu da oluşan son ürünü renklendirir ve toksik olmasına sebep olabilir. Örneğin, CuBr/bipiridin kalıntısı poli(metil metakrilat) yada polistireni kahverengiye boyarken, CuBr/alifatik amin ligand kompleksi ise yeşile boyar. Yıkama, sulu çözeltiyle ekstraksiyon, çözüp çöktürme ve polimeri çözüp alüminyum yada silica jel içeren kolondan geçirme gibi birçok yöntem son üründen katalizör uzaklaştırılması için geliştirilmiştir. Ama bu yöntemler genelde pahalı olamalarının yanında çok fazla katalizör sarfiyatına da sebep olur. Katalizör sarfiyatını azaltmak, geri kazanmak ve tekrar kullanmak için farklı katı destekli katalizör sistemleri geliştirilmiştir. Bu sistemler, katalizörün reaksiyon ortamında fiziksel olarak maddeye adsorplanması yada daha önceden sentezlenen çözünmeyen bir katı ligand ile kimyasal olarak kovalent bağ yapmasına dayanarak geliştirilmiştir. Katı bir yüzey üzerine kimyasal olarak immobilize edilen katalizörün kullanımı çok yönlüdür. Bu katı desteği olan maddeler genelde silika ya da türevleri ve süspansiyon polimerizasyonu sonucu elde

edilen çapraz bağlı polistiren kürecikleridir. Çoğunlukla, metil metakrilat ve stiren polimerizasyonu için bu katalizör sistemleri test edilmiştir.

Küçük monomer damlacıklarının süspansiyon ortamında dağıtılarak, polimerizasyonun bu ortamda gerçekleştirilebileceği düşüncesi, ilk olarak 1910 yılında ortaya atılmıştır. Süspansiyon polimerizasyonu günümüzde birçok ticari polimerin üretiminde kullanılmaktadır. Günümüzde akrilik ve metakrilik asitler, stiren ve kopolimerleri, vinil asetat, vinil klorür ve daha pek çok doymamış monomerin polimerizasyonunda kullanılan bir heterojen polimerizasyon tekniğidir. Düzgün küresel tanecik oluşturması nedeniyle teknik, boncuk ya da inci polimerizasyonu olarak da adlandırılır. Bu yöntemle ticari amaçlı üretilen ilk polimer olan vinil kloroasetat olmuştur. Süspansiyon polimerizasyonu, başlangıcından beri hızlı bir ilerleme göstererek günümüzde ticari öneme sahip poli(metil metakrilat), poli(vinil klorür), poli(vinil asetat) ve polistiren en çok bu yöntem ile elde edilmektedir. Polimerizasyon damlacık fazında serbest radikal polimerizasyonu seklinde ilerler. Genelde düşük oranlarda çapraz bağlayıcı organik moleküller kullanılarak küçük kürecikler seklinde çözünmeyen polimerler oluşturulur. Bu teknikte monomer veya monomerler sürekli karıştırma ile suda asılı damlalar halinde bulunur, böylelikle birbiri ile karışmayan iki ayrı faz oluşur. Dağıtma ortamı olarak genellikle su kullanılır. Polimerizasyon asılı damlacıklar içinde yürür. Bu arada su fazı, ısı transfer ortamı haline gelir. Damlaların çapı 10–100 μm mertebesindedir. Damlacıklar sıvı halden katı hale geçerken yapışkan bir hal alır. Viskozitesi gittikçe artan bu taneciklerin yapışmasını önlemek ve ortamın kararlılığını sağlamak için süspansiyon ajanlarından yararlanılır ve sürekli karıştırma uygulanır.

Bu oluşturulan moleküllerin ticari alanda kullanımı yaygındır. Örneğin, çeşitli modifikasyonlarla iyon değiştirici özelliği verilip kolon dolgu maddesi olarak sıkça kullanılır. Çevre kirliliği ve ekonomik açıdan, hidrometalurji ve diğer endüstrilerin atık sularında bulunan ağır metal iyonlarının miktarını azaltmak, metal iyonlarını uzaklaştırmak, geri kazanmak ve zenginleştirmek gerektiğinden, bu metal iyonlarını seçici, özel iyon değiştirici reçinelere ya da adsorbanlara duyulan ilgi artmaktadır.

Polimer-metal şelatlaması son yıllarda birçok araştırmacının ilgisini çekmiş ve birçok alanda başarıyla uygulanmıştır. Polimer-metal şelatlamasından yararlanarak polimer yüzeylere metal adsorpsiyonu da son yıllarda üzerine çok çalışılan konulardan birisidir. Bu tekniğe dayanan adsorpsiyonlar literatürde önemli yer tutmaktadır. Metal iyonlarının adsorpsiyonuna yönelik çalışmalarda adsorplayıcı olarak kullanılacak yüzeyin polimerlerle modifiye edildiği çalışmalar da mevcuttur. Çevreci ve daha ekonomik olmasından ve metal iyonlarıyla olan kuvvetli şelat yapılar oluşturmasından dolayı son yapılan çalışmalarda şelat polimerlerin atom transfer radikal polimerizasyonunda katı desteği olarak kullanılması yaygınlaşmıştır. Bu şelat polimerler yüzeylerine kimyasal olarak bağlanmış, genelde azot içeren liganlar içerirler ve metal tuzunu şelatlayarak kompleks oluştururlar ve polimerizasyonun sürekliliği bu katı ligand üzerinden yürür. Ayrıca, temel amaç olarak bu çalışmalarda katalizörü polimerden kolaylıkla ayrıştırmak, geri kazanmak ve tekrar kullanılıp kullanılamadığı ve etkinliğinin nasıl olduğu araştırılmıştır ve kayda değer veriler elde edilmiştir. Genellikle çapraz bağlı polistiren kürecik tabanlı ligandlar, yüksek sıcaklıkta çözünebilen ligand bağlı katı polimerler yada silika jel türevleri bu çalışmalarda katalizör desteği olarak metil metakrilatın atom transfer radikal polimerizasyonunda kullanılmıştır.

Yapılan bu çalışmada, süspansiyon polimerizasyonu ile elde edilmiş çapraz bağlı poliglisidil metakrilat küreciklerine kimyasal olarak *N,N,N',N'*-tetraetildietilentriamin bağlanmıştır (TEDETA). Sonrasında ise bu katı kürecikler stirenin atom transfer radikal polimerizasyonunda katı ligand olarak kullanılmıştır. Bu katalizör sistemini araştırmak için çeşitli reaksiyon parametreleri çalışılmıştır. Örneğin, katalizörün geri kazanımı ve sonrasındaki reaksiyonlarda rejenere edip ya da etmeden tekrar kullanılması, elde edilen polimerden tekrar bir polimerizasyon başlatılıp blok kopolimerizasyon yapılması çalışılmıştır. Rejenerasyon işlemi hem indigeyici ajanla hem de indirgeyici ajan ve CuBr katalizörü ile yapılmıştır.

Bütün durumlarda, polimerizasyon gerçekleşmiştir ve birinci derece kinetiğe uyduğu gözlemlenmiştir. Moleküler ağırlığı ve polidispersite açısından kontrollü polimerizasyon gözlenmesine rağmen, homojen ortamda yapılan reaksiyonlara göre düşük başlatıcı etkinliği elde edilmiştir. Molekül ağırlıkları beklenen molekül ağırlığı değerlerine göre yüksek elde edilmiştir. Polidispersite değerleri ise 1.8 ile 2.5 arasında elde edilmiştir. Katalizör kompleksinin yeniden kullanımı (2. ve 3. polimerizasyon) aşamasında aktivitenin düştüğü kinetik grafiklerinden görülmüştür. Bu düşen aktivite, sonrasında indirgen ajan olan parametoksi fenol kullanılarak yapılan rejenerasyon ile yükseltilmiştir, fakat yine azalan bir davranış göstermiştir. Katalizör kompleksinin geri kazanılarak yapılan toplam üç polimerizasyonda aynı aktivite ya da hız sabitine sahip olabilmesi için ek olarak CuBr ve indirgen ajan ile rejenerasyon çalışmaları yapılmış ve katalizör kompleksinin ikinci kullanımında birincisi ile aynı aktivite gösterdiği gözlemlenmiştir. Üçüncü kullanımda yine bir düşüş görülmüştür. Hedeflenen sonuca 1. ve 2. polimerizasyon kıyaslandığında; hem taze metal tuzu hem de indirgeyici ajan kullanılarak ulaşılmıştır. Sonrasında aktivite düşse dahi önceden yapılan geri kazanma ve rejenerasyon işlemlerine kıyasla daha az bir aktivite düşüşü gözlenmiştir. Yapılan tüm polimerizasyonlardaki düşen aktivitenin temel sebepleri sınırlı katalizör haraketliliği ve/ya da sterik etki ve polimer zinciri ile immobilize katalizör arasındaki uyumsuzluk olarak değerlendirilebilir. Ayrıyeten, katı ligandın üzerindeki CuBr'ün $CuBr_2$'ye yükseltgenmesi ve rejenerasyon sırasında indirgen ajanın bunu tekrar indirgeyecek kadar yeterli olmadığı yorumu yapılabilir. Buradan da halojen atomunun transferinin homojen atom transfer radikal polimerizasyonun'dakine göre daha az etkili olduğu sonucu çıkarılabilir. Sonuç olarak, kalitatif gözlemlere dayanarak metal katalizörünün tamamına yakını katı katalizör/ligand kompleksi desteğiyle polimer çözeltisinden uzaklaştırılmış ve oluşan polimerdeki renk kalıntıları elimine edilmiştir. Elde edilen bu katı ligand katı destekli atom transfer radikal polimerizasyonunda alternatif bir katalizör desteği olarak kullanıbilir.

1. INTRODUCTION

The transition-metal-mediated living polymerization (also named atom transfer radical polymerization, ATRP) is one of the most promising methods in the field of controlled/"living" radical polymerizations of vinyl monomers [1-9]. It is versatile for a wide variety of monomers, producing polymers with low polydispersities and well-controlled molecular weights, as well as end-functionalized polymers [10-13]. It also provides a useful approach for synthesizing novel polymer architectures such as star polymers [14-15], polymer brushes [16], nanoparticle hybrids [17], and polymer monolayers [18]. The most important advantage of ATRP is to have a great tolerance to water and other protonic species. In fact, polymerizations could be successfully carried out in water and other protonic species [19-20].

Although the advantages of ATRP are too much, catalyst residue causes some problems such as deeply coloring the resulting polymers (e.g., deep green using copper bromide-aliphatic amine). Previous studies show that catalyst residue can be removed from the product by silica gel or resin [21] or by re-precipitation into aqueous NH_4Cl [22]. Nonetheless, this post purification method does not only cost too much but also wastes catalyst. A possible solution to overcome these problems, several methods were developed to reduce the catalyst residue and to use catalysts again using supported catalysts on insoluble particles [23-28]. However, the heterogeneous systems cause some problems resulting a lack of control over polymerization. The ability of solid supported catalysts to mediate ATRP was much lower than that of their homogenous counterparts [23-25]. Resulting polymers had broad polydispersity values ($M_w/M_n \approx 1.5$ [25-26] or higher [23-24]), and the initiator efficiencies were generally low. This negative effect of the catalyst support on the polymerization has been based upon the limited catalyst diffusion occasioned by heterogeneity [23-28]. Unlike a small molecule, a polymer chain generally adopts random coil conformation in solution. The active ($P^{\cdot}$, radical) or dormant (P-Br) polymer ends embodied in the coils may have trouble in accessing the catalyst sites on the solid. A homogeneous support is thus preferred for ATRP.

Even though solid supported systems for ATRP were not very successful [24] supported copper halide via alkylpyridylmethanimine onto silica-gel/cross-linked polystyrene particles, the catalyst could not be washed out of the reactor. It can be said that is the great advantage to avoid catalyst loss from solid particles. This solid supported catalyst mentioned shortly before was used to perform polymerization of MMA with ethyl-2-bromoisobutyrate but did not show a good control over the molecular weight. In recent literature there are some examples of successful immobilization of catalyst that sustains their activity on solid support and especially on soluble support [29] where the catalyst was supported on PE-PEG molecule via tetraethyldiethylenetriamine (TEDETA) to polymerize MMA producing polymers with well-controlled molecular weight and very low polydispersity.

Chelating resins which were made of cross-linked polymeric beads synthesized by suspension polymerization, are designed for recovery and removal of heavy metal ions [30]. They are composed of a group of insoluble materials, which have ligands generally containing oxygen, nitrogen, sulfur, and phosphorus donor atoms on the material surface and are obtained by incorporation of ligands into the polymer matrix. The most popular one amongst these chelating resins are those containing nitrogen donor atoms which have high adsorption capacity and adsorption selectivity towards transition metal ions [31-34].

In this work, taking into account the properties of these type of chelating resins, *N*,*N*,*N'*,*N'*-tetraethyldiethylenetriamine functionalized cross-linked poly(glycidyl methacrylate-*co*-divinylbenzene) produced by conventional free-radical suspension polymerization was used as a supported ligand for CuBr to mediate the atom transfer polymerization of styrene. Recycle and regeneration of catalyst systems were further investigated.

2. THEORETICAL PART

2.1 Living Polymerization

Living polymerization was firstly described by Michael Szwarc in 1956 as a chain growth process without chain breaking reactions (transfer and termination) [35]. These chain breaking processes were avoided with the development of special high vacuum techniques to minimize traces (<1 ppm) of moisture and air in the anionic polymerization of non-polar vinyl monomers [36-37]. The techniques were first implemented in an academic setting but were quickly adapted on an industrial scale, which ultimately led to the mass production of several commercial products, most notably well-defined block copolymers capable of performing as thermoplastic elastomers [38].

The synthesis of such copolymers by living anionic polymerization demands fast initiation and relatively slow propagation in order that the distribution of block lengths be controlled. These requirements can be achieved with the use of alkyl lithium initiators in non-polar solvents via the formation of ion pairs or their aggregates. Polymerization ensures end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not provide for molecular weight control narrow molecular weight distributions (MWD). Additional prerequisites to achieve these goals are that the initiator should be consumed at early stages of polymerization and that exchange between species of various reactivities is fast comparison with propagation. If these additional criteria are met, a controlled polymerization results. Polymerization can also be defined as controlled if side reactions occur, but only to an extent which does not considerably disturb the control of the molecular structure of the polymer chain [38-42]. Therefore, to overcome the problems a new idea is discovered for radical polymerization which is called controlled radical polymerization.

Michael Szwarc not only contributed to the development of anionic polymerization but was also involved throughout the 1950s in detailed studies of radical processes [43-50]. While living anionic vinyl polymerization was being discovered and developed, conventional radical polymerization was already flourishing. Many new products were commercialized, and a comprehensive theory of radical polymerization was developed [41, 51-54].

2.2 Controlled / Living Radical Polymerization

Today, conventional free-radical polymerization (FRP) is still one of the most widely applied processes for the preparation of polymeric materials as nearly 50% of all commercial synthetic polymers are produced by this method. The main reason for this fact is that a wide range of monomers can be polymerized and copolymerized via radical chemistry, which provides a spectrum of materials for various markets. Moreover, the polymerization does not require rigorous process conditions. On the other hand, some important elements of the polymerization process that would lead to the well-defined polymers with controlled molecular weight, polydispersity, composition, structural architecture, and functionality are poorly controlled. The importance of the synthesis of polymers with such control has been augmented due to the rising demands for the specialty polymers. Obviously, living polymerization is an essential technique for synthesizing polymers with controlled structures. Moreover, living polymerization techniques allow preparation of macro monomers, macro initiators, functional polymers, block and graft copolymers, and star polymers. In this way, the need for specialty polymers having a desired combination of properties can be fulfilled. Control of complex architectures by living polymerization has largely been achieved using living anionic and cationic as well as group transfer polymerization techniques. From the practical point of view, however, these techniques are less attractive than free-radical polymerization, because the latter can be performed much more easily. Moreover, ionic techniques are limited to a very few vinyl monomers, whereas practically all vinyl monomers can be homo and copolymerized by a free-radical mechanism long-lasting goal has been the development of controlled/living radical polymerization methods. As mentioned previously, radical polymerization suffers from some defects (i.e., the control of the reactivity of the polymerizing monomers and, in turn, the control of the structure of

the resultant polymer). In ionic living systems, however, the chain ends do not react with one another due to the electrostatic repulsion. On the other hand, the growing radicals very easily react with each other at diffusion-controlled rates via combination and/or disproportionation. Therefore, controlled/living radical polymerization has long been considered impossible. Following the discovery of living anionic and cationic polymerization, many attempts have been made to find controlled/living radical polymerization systems to achieve a high level of control over molar mass, polydispersity, end groups, and architecture. Despite considerable progress, a truly controlled/living radical polymerization has not been developed until a little more than a decade ago. In the past decade, a number of controlled/living radical polymerization methods have been developed and the three most promising types are atom transfer radical polymerization (ATRP) (also known as transition metal catalyzed radical polymerization), stable free radical polymerization (SFRP) (also known as nitroxide-mediated polymerization, NMP), and reversible addition-fragmentation chain transfer (RAFT) polymerization. This chapter focuses on the recent progress on these three methods and the earlier attempts will not be considered here as they were discussed in detail in the first edition of the book [55].

2.2.1 ATRP

Atom transfer radical polymerization is a controlled/"living" polymerization based on the use of radical polymerization to convert monomer to polymer. An alternative was sought because other types of living polymerizations are severely limited by many factors: only a small number of monomers can be used, the reactions are sensitive to moisture, and two or more monomers cannot be randomly copolymerized. Radical polymerization, in contrast, can polymerize hundreds of monomers, can copolymerize two or more monomers, and can be performed in water as emulsions or suspensions. Controlled/"living" radical polymerization promised to overcome these limitations and provide a method to maximize the potential of living polymerizations.

In 1995, Matyjaszewski and Sawamoto were the first to develop a transition-metal mediated controlled/''living" radical polymerization that used a simple, inexpensive polymerization system [5, 56]. It is capable of polymerizing a wide variety of monomers, is tolerant of trace impurities (water, oxygen, inhibitor), and is readily

applicable to industrial processes. The system that was developed was termed ‘atom transfer radical polymerization’ (ATRP).

The control of the polymerization afforded by ATRP is a result of the formation of radicals that can grow, but are reversibly deactivated to form dormant species. Reactivation of the dormant species allows the polymer chains to grow again, only to be deactivated later. Such a process results in a polymer chain that slowly, but steadily, grows and has a well-defined end group (for ATRP that end group is usually an alkyl halide).

A general mechanism for ATRP is shown in Figure 2.1. ATRP is based on the reversible homolytic cleavage of carbon-halogen bond by a redox reaction. The propagating species P_n^*, are generated through by a transition metal complex (activator, M_t^n –Y / ligand, where Y may be another ligand or a counter ion) that undergoes a one-electron oxidation with concomitant abstraction of a (pseudo) halogen atom, X, from a dormant species, P_n–X. Radicals react reversibly with the oxidized metal complexes, $X–M_t^{n+1}$/ ligand, the deactivator, to reform the dormant species and the activator.

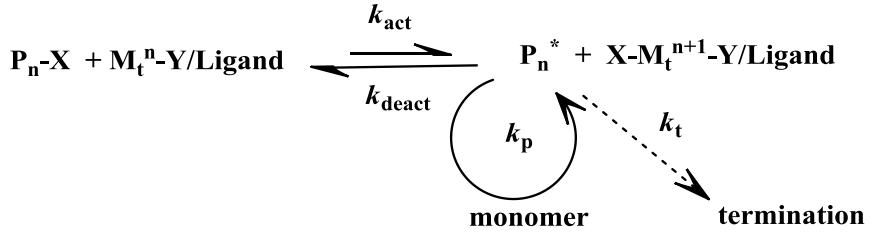

Figure 2.1 : General mechanism of ATRP.

These processes are rapid, and the dynamic equilibrium that is established favors the dormant species that occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}, respectively. By this way, all chains can begin growth at the same time, and the concentration of the free radicals is quite low, resulting in reduced amount of irreversible radical-radical termination. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer

chains undergo termination. Other side reactions may additionally limit the achievable molecular weights.

ATRP remains the most powerful, versatile, simple, and inexpensive. Only ATRP has been able to polymerize a wide range of monomers including various styrenes, acrylates and methacrylates as well as other monomers such as acrylonitrile, vinyl pyridine, and dienes. ATRP commonly uses simple alkyl halides as initiators and simple transition metals (iron, copper) as the catalysts. These catalysts can be used in very low amounts, whereas, other controlled polymerization systems require the use of expensive reagents in much higher concentrations.

2.2.1.1 Kinetics of ATRP

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator ($X\text{-}M_t^{n+1}$/Ligand). The rate equation of copper-based ATRP is formulated in discussed conditions and given in (2.1). The apparent propagation rate constant, where k_p and K_{eq} refer to the absolute rate constant of propagation and the atom transfer equilibrium constant for the propagating species, respectively.

$$R_p = k_p^{app}\,[M] = k_p\,[R\bullet]\,[M] = k_p K_{eq}\,[I]\,([CuX]/[CuX_2])\,[M] \qquad \textbf{(2.1)}$$

Figure 2.2 shows a typical linear variation of conversion with time in semi logarithmic coordinates (kinetic plot). Such a behavior indicates that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer.

However, since termination occurs continuously, the concentration of the Cu(II) species increases and deviation from linearity may be observed [57]. For the ideal case with chain length independent from termination, persistent radical effect [58-59] kinetics implies the semi logarithmic plot of monomer conversion vs. time to the 2/3 exponent should be linear. Nevertheless, a linear semi logarithmic plot is often observed.

This may be due to an excess of the Cu(II) species present initially, a chain length dependent termination rate coefficient, and heterogeneity of the reaction system due to limited solubility of the copper complexes.

It is also possible that self-initiation may continuously produce radicals and compensate for termination. Similarly, external orders with respect to initiator and the Cu(I) species may also be affected by the persistent radical effect [60].

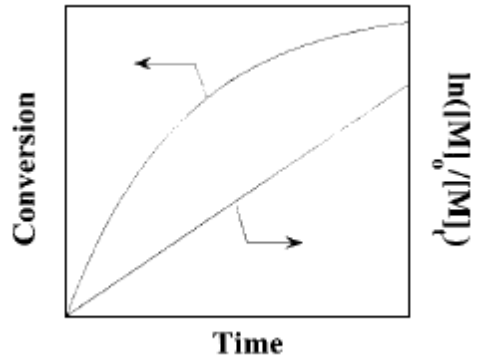

Figure 2.2 : Kinetic plot and conversion vs time plot for ATRP.

Results from kinetic studies of ATRP for styrene (St) [61], methyl acrylate (MA) [62] and methyl methacrylate (MMA) [63-64] under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations. These observations are all consistent with the derived rate law.

It should be noted that the optimum ratio can vary with regard to changes in the monomer, counter ion, ligand, temperature, and other factors [3, 63, 65]. The precise kinetic law for the deactivator CuX_2 was more complex due to the spontaneous generation of Cu(II) via the persistent radical effect [58, 60-61].

In the atom transfer step, a reactive organic radical is generated along with a stable Cu(II) species that can be regarded as a persistent metallo-radical. If the initial concentration of deactivator Cu(II) in the polymerization is not sufficiently large to ensure a fast rate of deactivation (k_d[Cu(II)]), then coupling of the organic radicals will occur, leading to an increase in the Cu(II) concentration.

Radical termination occurs rapidly until a sufficient amount of deactivator Cu(II) is formed and the radical concentration is low. Under such conditions, the rate at which radicals combine (k_t) will become much slower than the rate at which radicals react with the Cu(II) complex in a deactivation process and a controlled polymerization will proceed.

Typically, a small fraction (~5 %) of the total growing polymer chains will be terminated during the early stage of the polymerization, but the majority of the chains (>95 %) will continue to grow successfully.

The effect of Cu(II) on the polymerization may additionally be complicated by its poor solubility, by a slow reduction by reaction with monomers leading to 1,2-dihalo adducts, or from the self-initiated systems such as styrene and other monomers.

If the deactivation does not occur, or if it is too slow ($k_p >> k_d$), there will be no control and polymerization will become classical redox reaction therefore the termination and transfer reactions may be observed. To control the polymerization better, addition of one or a few monomers to the growing chain in each activation step is desirable. Molecular weight distribution for ATRP is given in equation (2.2), where "p" is polymerization yield, $[RX]_0$ is concentration of the functional polymer chain, $[X\text{-}M_t^{n+1}]$ states concentration of the deactivators, k_d and k_p indicate rate constant of deactivation and rate constant of polymerization, respectively.

$$M_w/M_n = 1 + ((k_d[RX]_0)/(k_p[X\text{-}M_t^{n+1}])) \times ((2/p)-1) \qquad \textbf{(2.2)}$$

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

a) For the smaller polymer chains, higher polydispersities are expected to be obtained because the smaller chains include little activation-deactivation steps and also the chain length difference is higher for small polymer chains resulting in little control of the polymerization.

b) For the higher ratios of k_p/k_d, higher polydispersities (molecular weight distributions) are usually obtained resulting in the little control of polymerization.

c) Resulting molecular weight distribution decreases as the concentration of the deactivators increases [57].

2.2.1.2 Components of ATRP

As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo) halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration.

Monomers

Monomers: In ATRP, a variety of monomers, such as styrenes, (meth)-acrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and diens can be used to obtained well-defined polymers. However, even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species [66].

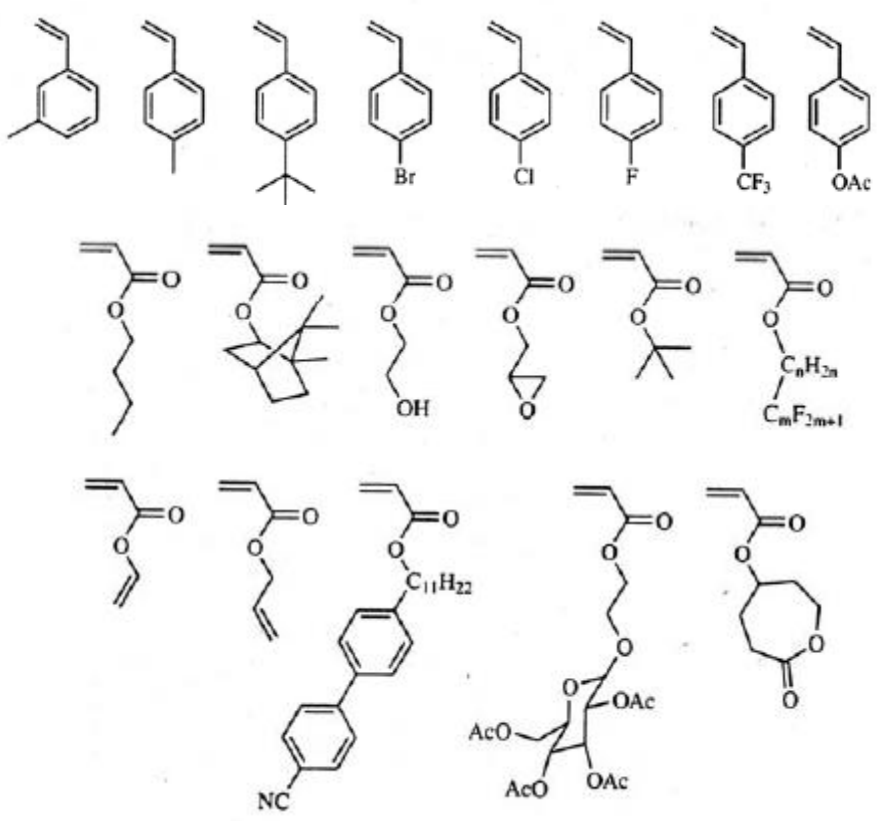

Figure 2.3 : Some of the monomers used in ATRP.

Initiators

Organic halides having a labile carbon-halogen bond are the most successfully employed initiators in ATRP. In general, these organic halides possess electron withdrawing groups and/or atoms such as carbonyl, aryl, cyano, or halogens at α-carbon to stabilize the generated free radicals. The common way to initiate is via the reaction of an activated (alkyl) halide with the transition-metal complex in its lower oxidation state. To obtain well-defined polymers with narrow molecular weight distributions, the halide atom, X, should rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is best. Iodine works well for acrylate polymerizations in copper-mediated ATRP and has been found to lead to controlled polymerization of St in ruthenium and ruthenium-based ATRP [67-69]. The carbon–fluorine bond strength is too strong for the fast activation–deactivation cycle with atom transfer. To obtain similar reactivity of the carbon-halogen bond in the initiator and the dormant polymer end, the structure of the alkyl group, R, of the initiators should be similar to the structure of the dormant polymer end. Typical examples would be the use of ethyl 2-bromoisobutyrate and a Cu(I) complex for the initiation of a methacrylate polymerization [70], or 1-phenylethyl chloride for the initiation of a styrene polymerization [2]. In addition, Percec and co-workers reported the use of sulfonyl chlorides as universal initiators in ATRP [71]. Also the use of di-, tri-, or multifunctional initiators is possible, which will result in polymers growing in two, three, or more directions. Besides, some pseudo halogens, specifically thiocyanates and thiocarbamates, have been used successfully in the polymerization of acrylates [72]. The alternative way to initiate ATRP is via a conventional free-radical initiator, which is used in conjunction with a transition-metal complex in its higher oxidation state. Typically one would use AIBN in conjunction with a Cu(II) complex. Upon formation of the primary radicals and/or their adducts with a monomer unit, the Cu(II) complex very efficiently transfers a halogen to this newly formed chain. In doing so the copper complex is reduced, and the active chain is deactivated. This alternative way of initiation was termed “reverse ATRP” [73].

Catalyst and transition metals

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. The metal center must have at least two readily accessible oxidation states separated by one electron. The metal center should have reasonable affinity toward a halogen. The coordination sphere around the metal should be expandable on oxidation to selectively accommodate a (pseudo) halogen. The ligand should complex the metal relatively strongly. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species. A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe, Ni, Ru, etc. have been used to some extent [57, 74].

Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal, should also allow expansion of the coordination sphere, and should allow selective atom transfer without promoting other reactions. The most common ligands for ATRP systems are substituted bipyridines, alkylpyridyl methanimines and multidentate aliphatic tertiary amines such as N,N,N′,N″,N″ pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino)ethyl]amine (Me_6-TREN) [2, 4]. In addition to those commercial products, it has been demonstrated that hexamethyltriethylenetetramine (HMTETA) provides better solubility of the copper complexes in organic media and entirely homogeneous reaction conditions [61]. Since copper complexes of this new ligand are almost insoluble in water, ATRP technique can be employed in preparing poly(acrylate esters) in aqueous suspension [75].

Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers.

Temperature and reaction times

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of the higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control ("livingness") may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures. The optimal temperature depends mostly on the monomer, the catalyst, and the targeted molecular weight. Therefore, for successful ATRP, optimum temperature should be found depending on the monomer, catalyst and the other components of ATRP [57].

2.3 Suspension Polymerization

Suspension polymerization is composed of a series of processes, all of which comprise emulsifying monomers to droplets by using mechanical agitation to mix them in a suspending medium in which they are insoluble in the presence of a free-radical initiator. Drops of a monomer-containing phase including free-radical initiator are dispersed in a continuous liquid phase and polymer is produced inside the drops. The monomer phase sometimes contains no diluent and the chemical reactions, which occur inside the drops, are very similar to the reaction named bulk polymerization. In most cases, polymer is formed by a chain reaction mechanism. This process is used in the production of many commercial resins, including polyvinyl chloride (PVC), a widely used plastic, styrene resins including polystyrene, expanded polystyrene, and high-impact polystyrene, as well as poly(styrene-acrylonitrile) and poly(methyl methacrylate) [76-78].

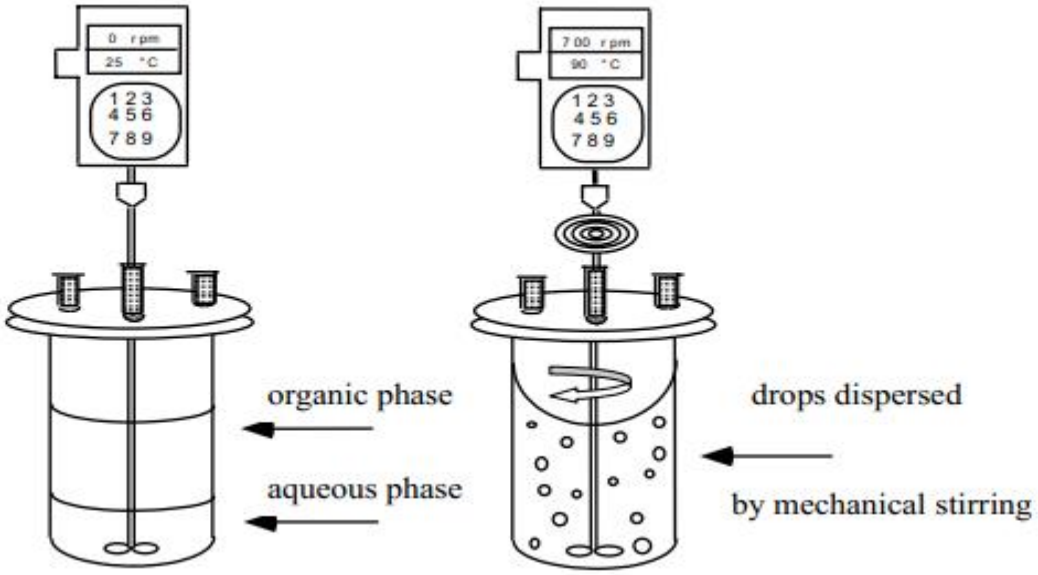

Figure 2.4 : Schematic representation of suspension polymerization.

The reaction mixture includes two phases, a liquid matrix (aqueous phase) and monomer droplets (organic phase). The monomer and initiator are not soluble in the liquid phase, so monomer droplets are formed when agitation is applied within the liquid matrix. A suspension agent is usually added to assist the formation of the initial monomer emulsion and to stabilize the formed monomer drops in order not to come together [79]. General schematic representation is shown in Figure 2.4. The dispersants so-called Pickering emulsifiers involve either macromolecules which are insoluble in the suspending medium or usually inorganic insoluble powders [80-81]. The reaction mixture generally has a volume ratio of monomer to liquid phase of 0.1 to 0.5. The aqueous phase acts like a heat transfer agent and it enables high rates of polymerization with little change in the temperature of the polymerizing solution. The reactions are usually carried out in tank reactor equipped with mechanical stirrer that helps to keep the monomer droplets separated and creates a more uniform suspension. Continuous stirring leads to a more narrow size distribution of the final polymer beads. The resulting bead particles in suspension polymerization have approximately the same size as the original monomer droplets with diameters on the order of 10-3 to 0.5 cm [79].

2.3.1 Cross-linked polymeric beads

Cross-linked polymer beads are a class of polymer beads, which are synthesized by conventional suspension polymerization, where mono and polyvinyl monomers (crosslinking agent) react in the presence of a porogen agent (inert diluent). One of the characteristics of this phenomenon is to form a porous structure that is related with the type and concentration of diluents and monomers used. Moreover, It depends on temperature and stirring, as well [82-86]. These polymeric beads are composed of a permanent well-developed porous structure and perfect spherical shape (Figure 2.5) in the dry state, have a wide range of applications, for example, support for catalysts, immobilization of enzymes, HPLC columns and etc [87-90].

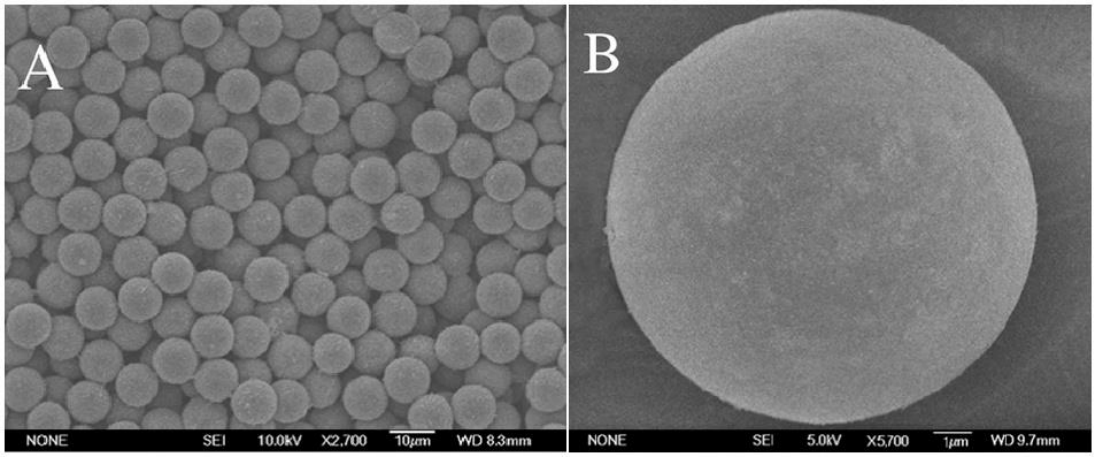

Figure 2.5 : SEM picture of polymeric beads synthesized by suspension polymerization method. (A) overall appearance of cross-linked beads, (B) outer surface of those beads [91].

2.3.2 Chelating resins

Chelating resins which are synthesized for preconcentration of metal ions, separation and adsorption are widely used in the recovery and removal of metal ions from waste water and for analyzing of trace metal ions [92-94]. They are mostly insoluble materials that have ligands containing oxygen, nitrogen, sulfur, and phosphorus donor atoms in order to bond with metal ions and are successfully made by incorporation of ligands into the polymer matrix. The most popular one amongst chelating resins contains nitrogen atoms that have high adsorption capability and most selectivity to transition metal ions by forming complex readily [30, 95].

3. EXPERIMENTAL PART

3.1 Chemicals

Glycidyl methacrylate (GMA, 97%) and *N*,*N*,*N*′,*N*′-Tetraethyldiethylenetriamine (TEDETA, 90%, Figure 3.1) were purchased from Sigma-Aldrich. *N*,*N*,*N*',*N*'',*N*''-Pentamethyldiethylenetriamine (PMDETA, 99%) and divinylbenzene (DVB) were purchased from Merck. Copper (I) bromide (CuBr, 99.99%), was purchased from Alfa Aesar. Styrene (St, 99%), methyl methacrylate (MMA, 99%), ethyl-2-bromopropionate (EBrP) was purchased from Acros Organics Co.. p-methoxy phenol (99%,) was purchased from Janssen. Tetrahydrofuran (THF), 1,4-dioxane (DO)**,** toluene, n-heptane**,** dichloromethane (DCM), methanol were purchased from J.T. Baker Co. Polyvinylpyrrolidone (PVP) and benzoyl peroxide (BPO) were industrial product. All reagents were used without further purification.

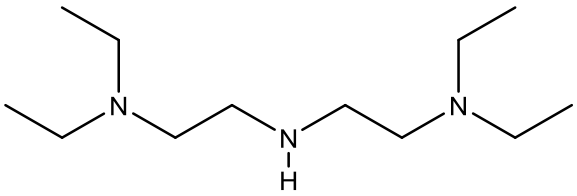

Figure 3.1 : *N*,*N*,*N*′,*N*′-Tetraethyldiethylenetriamine.

3.2 Synthesis of Cross-linked Ligand

3.2.1 Synthesis of GMA-DVB cross-linked copolymer beads

Poly(glycidyl methacrylate-*co*-divinylbenzene) (GMA-*co*-DVB) copolymer beads were synthesized by radical suspension polymerization similar with reported in the literature earlier [30]. In 250 mL three-necked flask, the monomer phase consisting of 7.42 mL of GMA (80%), 2 mL of DVB (20%), 0.15 g initiators (BPO), and 10 mL of diluents (8 mL toluene and 2 mL n-heptane) was suspended in the aqueous phase containing 60 mL of water, 2.8 g of NaCl, and 0.15 g PVP as stabilizer. The polymerization was carried out at 80 ^{o}C for 4 h under 500 rpm stirring rate. After

completion of the reaction, the copolymer beads were filtered and washed well with water and then methanol, kept in methanol for one day further and dried under vacuum at 50 ^{o}C. The product, then called "X-PGMA", in perfect spherical beads was sieved and used for further reactions. (Figure 3.2)

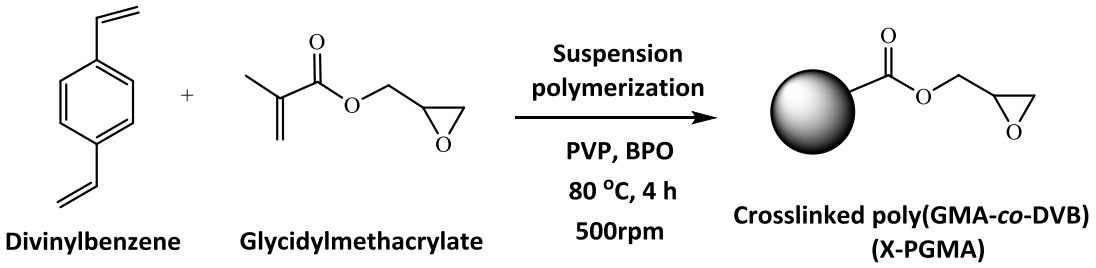

Figure 3.2 : Synthesis of poly(glycidyl methacrylate-*co*-divinylbenzene) beads.

3.2.2 Synthesis of TEDETA attached X-PGMA

Attachment of multimodal TEDETA ligand on X-PGMA beads is basically based on epoxy ring opening reaction (Figure 3.3). The reaction was performed in a reactor (100 mL). Cross-linked bead sample and DO (10 mL) were transferred in the flask then certain amount of TEDETA ligand was added to this mixture, and was stirred at 75 ^{o}C. Parameters are shown in details in Table 3.1. The ligand-attached beads were collected by filtration and washed with excess water. The product was cleaned with DO and dried under vacuum at 50 ^{o}C for 24 h. The fresh insoluble ligand samples named XL-1, XL-2, and XL-3.

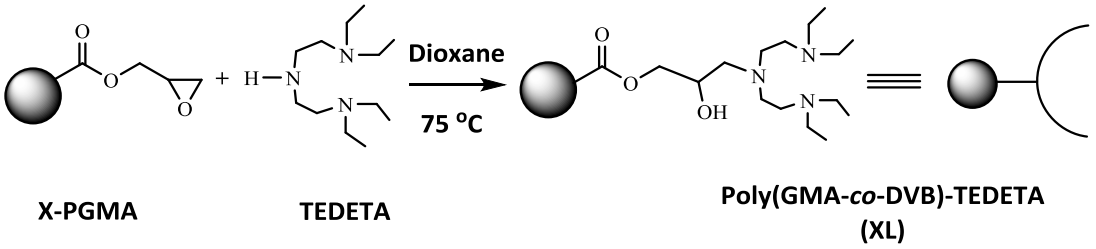

Figure 3.3 : Attachment of multimodal TEDETA ligand onto X-PGMA.

Table 3.1 : Reaction parameters of TEDETA attachment onto X-PGMA.[a]

Run	Cross-linked bead			TEDETA (mmol)	Time (day)
	Sample	Size (μm)	Amount (g)		
XL-1	X-PGMA-1	422-590	2	6.38	4
XL-2	X-PGMA-2	251-422	2	4.48	4
XL-3	X-PGMA-3	251-422	2	5.63	2

a: At 75 ^{o}C in 10 mL of DO.

3.3 Styrene Polymerization Using Solid Supported Ligand

3.3.1 Catalyst recycle without regeneration

A typical ATRP procedure was performed as follows. Catalyst, CuBr (0.0626 g, 0.436 mmol), and ligand, XL-1 (0.538 g, containing 0.436 mmol TEDETA) were placed in a 48 ml of flask, which contained a side arm with a Teflon valve sealed with a Teflon stopper. Then the flask was deoxygenated by vacuum-nitrogen cycles three times. The degassed St (10 mL, 87.3 mmol), 2 mL of toluene were then introduced by syringe then mixture was stirred at 500 rpm. Finally, initiator EBrP (56 μL, 0.436 mmol) was added by dropwise then the flask was replaced in thermostatically controlled oil bath at 110 °C and 500 rpm stirring rate. Reaction mechanism is shown in Figure 3.4. After that, the reaction was performed for 2 h and the slightly yellow XL-1 then turned green in 20 minutes (Figure 3.5). At the end of the reaction, metal/XL-1 complex was filtered and removed from polymer solution, which was then analyzed in GPC to determine molecular weight and distribution.

Control reaction without TEDETA ligand was carried out in the above polymerization conditions using X-PGMA-1 bead (0.36 g, containing 0.436 mmol epoxide groups) instead of XL-1 ligand.

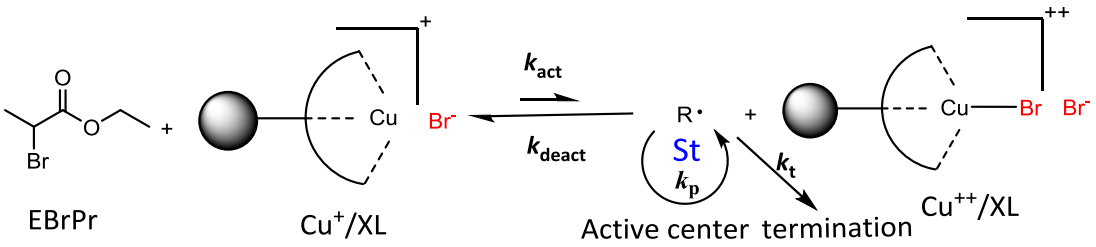

Figure 3.4 : Mechanism of ATRP with XL.

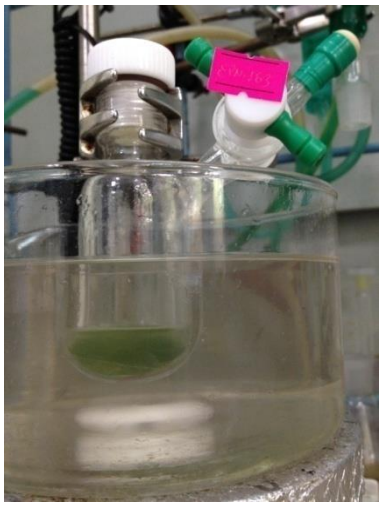

Figure 3.5 : Photo of the reaction after 20 minutes showing green beads.

After the polymerization was completed, filtered metal/XL-1 complex was washed well with toluene and dried in vacuum oven for overnight at 50 ^{o}C. Then, dry complex was placed in flask again and the same amounts of degassed styrene, toluene and initiator as in the first run were added to flask and reheated to 110 °C (marked as second run). This procedure was repeated two times further (third and fourth run, respectively).

3.3.2 Block copolymerization

In order to perform block copolymerization, polystyrene sample (0.5 g, containing roughly 0.0385 mmol active Br endings according to GPC results) as macro initiator synthesized in second run mentioned above, CuBr (0.0154 g, 0.107 mmol), XL-3 (0.12 g, containing TEDETA 0.107 mmol), and toluene (4 mL) were added to a schlenk flask and degassed as described above. Then, degassed MMA (0.575 mL, 5.373 mmol) were added. The mixture was immersed in a 90 °C oil bath for 3.5 h. Another reaction was performed using soluble ligand PMDETA (22.44 µL, 0.107 mmol) and with the same amount of reactants above (PS, CuBr, toluene and MMA)

in the same conditions. Both of the mixtures were precipitated in methanol then filtered and dried in oven. Polymers were analyzed by ^{1}H NMR spectroscopy to determine conversion and by GPC to calculate molecular weight.

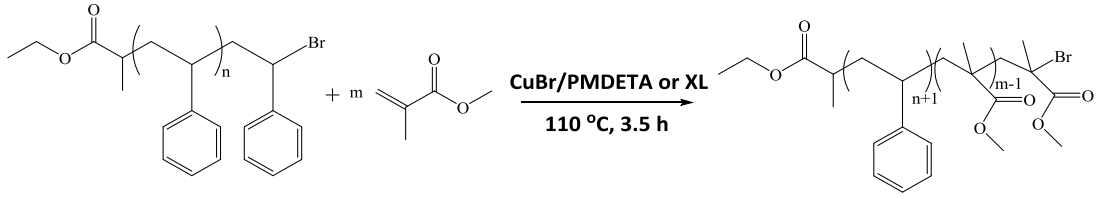

Figure 3.6 : Synthesis of PS-*block*-PMMA.

3.4 Kinetic Studies of Styrene Polymerization Using Solid Supported Ligand

3.4.1 Catalyst recycle without regeneration

In a typical polymerization run, CuBr (0.047 g, 0.3273 mmol), XL-2 (0.3008 g, containing 0.3273 mmol TEDETA), and toluene (1 mL) were charged to a Schlenk flask and degassed with several vacuum/nitrogen cycles. Then degassed St (5 mL, 43.6 mmol) was introduced by syringe and stirred. After the XL-2 support was thoroughly dispersed, degassed EBrP (28 μL, 0.218 mmol) was added by dropwise to the mixture while stirring. Then the flask was immersed in an oil bath (110 °C) for polymerization. The polymerization solution (0.1-0.2 mL) was withdrawn at different intervals to analyze the conversion by GC. Only the last sample were taken and analyzed by GPC to calculate molecular weight.

After the polymerization completed, the flask was lifted from the oil bath. The green XL-2 was carefully removed by filtering, washed well with 20 mL of toluene, and dried for 24 h in a vacuum oven at 50 ^{o}C. To perform second cycle, metal/XL-2 complex weighting (0.3573 g) was then placed in the flask. The same amounts of degassed St, toluene, and initiator as in the first run were added to the flask and reheated to 110 °C. After that, third cycle was further performed with metal/XL-2 (0.3824 g) from second cycle.

3.4.2 Catalyst recycle with regeneration using reducing agent

A typical polymerization procedure was as follows: CuBr (0.047 g, 0.3273 mmol), XL-3 (0.3648 g, containing TEDETA 0.3273 mmol), and toluene (1 mL) were added to a Schlenk flask and degassed by several vacuum-nitrogen cycles. Degassed styrene (5 mL, 43.6 mmol) was then added to the flask by a nitrogen-purged syringe. After the XL-3 support was thoroughly dispersed, degassed initiator (EBrP, 28 μL, 0.218 mmol) was added by dropwise to the flask while stirring. The flask was subsequently placed to 110 °C in an oil bath. The polymerization solution (0.1-0.2 mL) was withdrawn at different intervals to analyze the conversion by GC and molecular weight by GPC.

After the polymerization completed, the flask was lifted from the oil bath. The green XL-3 was carefully removed by filtering, washed well with 20 mL of toluene, and dried for 24 h in a vacuum oven at 50 ^{o}C. To perform second cycle, metal/XL-3 (0.4462 g) and p-methoxy phenol (0.0732 g, 0.589 mmol) as reducing agent (RA) were then placed in the flask. The same amounts of degassed St, toluene, and initiator as in the first run were added to the flask and reheated to 110 °C. After that, third cycle was further performed with metal/XL-3 (0.5146 g) and p-methoxy phenol (0.1063 g, 0.856 mmol) placed in the flask. The same procedure as in the second one was repeated.

3.4.3 Catalyst recycle with regeneration using both reducing agent and fresh catalyst

As distinct from the reaction with only reducing agent mentioned above, additional fresh CuBr catalyst was used in second and third cycle. For the first cycle, the same amounts of XL-3, styrene, EBrP and toluene were used and again the same procedure was performed as in the above. To perform second cycle, dried metal/XL-3 complex (0.442 g), fresh catalyst CuBr (0.006 g, 0.042 mmol), reducing agent p-methoxy phenol (0.047 g, 0.378 mmol) were then placed in the flask. The same amounts of degassed St, toluene, and initiator as in the first run were added to the flask and placed to oil bath at 110 °C. After that third cycle was further performed. To perform third cycle, metal/XL-3 (0.5156 g), CuBr (0.006g, 0.042 mmol) and p-methoxy phenol (0.1087 g, 0.876 mmol) were then placed in the flask.

3.5 Characterization Methods

3.5.1 Infrared spectrometer

FT-IR spectra were recorded on a Thermo Nicolet 6700 FT-IR spectrometer to characterize X-PGMA and XL.

3.5.2 Gel permeation chromatography (GPC)

The GPC system is equipped with an Agilent model isocratic pump, guard and one Waters Styragel columns, and a Viscotek TDA 302 triple dedector (RI, dual laser light scattering (LS) (λ= 670 nm, 90° and 7°) and a differential pressure viscometer). TD-GPC (Figure 3.7) was conducted to measure the molecular weights in THF with a flow rate of 1.0 mL/min at 30 °C. RI dedector was calibrated with different PS standards having narrow molecular weight distribution (in the range of 1050 and 400000 g/mol at 30 °C in THF, d*n*/dc= 0.185 mL/g) provided by Viscotek company. Data analyses were performed with OmniSec 4.5 software from Viscotek Company.

Figure 3.7 : Triple dedector GPC and autosampler.

3.5.3 Gas chromatography (GC)

Monomer conversions were determined using a Perkin Elmer AutoSystem XL gas chromatography (GC) equipped with an FID detector using a SGE-G4 capillary column (30 m length, 0.25 mm ID, 0.25 μm film thickness). Injector and detector were kept constant at 280 and 285 ^{o}C, respectively. Analysis was carried out isothermally starting from 40 ^{o}C holding for 1 min followed by an increased temperature to 200 ^{o}C at a heating rate of 40 ^{o}C/min and holding at 200 ^{o}C for 1 min. Conversions were calculated by detecting the decrease of the monomer peak areas (monomer consumption) relative to the peak areas of toluene as an internal standard.

3.5.4 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR measurements (Figure 3.8) were recorded in d_1-$CDCl_3$, using an Agilent VNMRS500 (500 MHz) instrument.

Figure 3.8 : Agilent VNMRS500 NMR instrument.

4. RESULTS AND DISCUSSION

4.1 Synthesis of Cross-linked Ligand

Attachment of TEDETA onto poly(GMA-*co*-DVB) (named X-PGMA) which were completely white before, yielded slightly yellow colour both in solution and on the new solid ligand surface. The reaction was taken 2 to 4 days, because there was heterogeneous and dilute medium and solvent was used to disperse solid particles.

In order to prove qualitatively if TEDETA chemically was bounded to X-PGMA samples, FT-IR measurements were done after quantitative calculations on samples using gravimetric techniques. Figure 4.1 shows the FTIR spectra of the X-PGMA and XL beads. The band because of ester vibrations at 1723 cm^{-1} corresponds to the >C=O stretching vibration. The epoxy peaks found in spectra of initial poly(GMA-*co*-DVB) sample, at around 841 cm^{-1} and 906 cm^{-1} (epoxy ring vibrations), 1451 cm^{-1} [δ (CH) epoxy] have not totally disappeared from spectra of sample modified with TEDETA, poly(GMA-*co*-DVB)-TEDETA, showing incomplete conversion of the epoxy groups. Nominately, some parts of epoxy groups usually remain inside the cross-linked polymer, being inaccessible for subsequent reactions. The similar was observed for poly(GMA-*co*-EGDMA) modified with ethylenediamine [96].

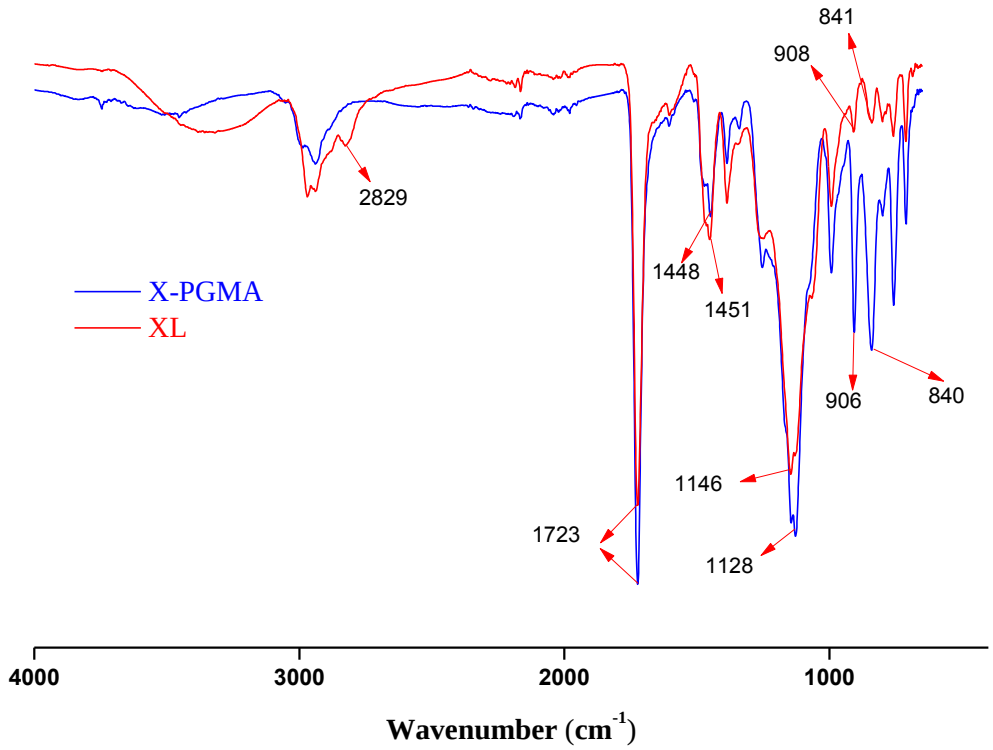

Figure 4.1 : FTIR spectra of X-PGMA and XL beads.

Incorporation of TEDETA on X-PGMA showed very few marked change in the FT-IR spectrum of poly(GMA-*co*-DVB)-TEDETA. To give an example, the bands characteristic for the cross-linked copolymer at between 2930 cm^{-1} and 2970 cm^{-1} showed slight changes in modified sample. Another change in those spectra of XL is observed very broad band at 3100 cm^{-1} and 3600cm^{-1} range can be considered as O-H vibration band arising from ring opening reaction of the epoxy function. Moreover, the weak band arising around 2830 cm^{-1} can be assigned to C-H stretching vibration due to attached TEDETA onto cross-linked polymer. It is shown that the peaks of XL below 1000 cm^{-1} have lower intensity than that of X-PGMA.

After qualitative measurements on samples using FT-IR, quantitative calculation was carried out using gravimetric measurements. According to gravimetric measurements, weight increment was observed for each XL sample. XL-1, XL-2 and XL-3 were weighted as 2.42 g, 2.61 g and 2.48 g, respectively. That obviously indicated the TEDETA ligand was successfully bonded onto X-PGMA beads. Table 4.1 and Table 4.2 show the summary of cross-linked ligand synthesis and how many amount of multimodal ligand, TEDETA, was attached to each sample, respectively. As seen on table, even though reaction time of XL-1 and XL-2 is same and initial

TEDETA amount for XL-1 is more than XL-2, loaded TEDETA is high on XL-2. This may be due to the particle size of first bead sample (422-590 μm) was larger than others were. The higher particle size means lower surface area. That might have caused few amount of TEDETA bonded onto XL-1. The different TEDETA amounts found for XL-2 and XL-3 can be easily associated with reaction time rather than feed amount.

Table 4.1 : Summary of cross-linked ligand synthesis.

Run	**Cross-linked bead**		**TEDETA (mmol) (% amount of GMA) (Feed)**	**Time (day)**
	Sample	Amount (g)		
XL-1	X-PGMA-1	2 (11.2 mmol GMA)	6.38 (60%)	4
XL-2	X-PGMA-2	2 (11.5 mmol GMA)	4.48 (40%)	4
XL-3	X-PGMA-3	2 (11 mmol GMA)	5.63 (50%)	2

Table 4.2 : Results of cross-linked ligand synthesis.

Run	**Amount (g)**	**TEDETA (mmol) (Found)**	**mmol TEDETA/g bead**
XL-1	2.42	1.96	0.81
XL-2	2.61	2.85	1.10
XL-3	2.48	2.22	0.90

All in all, it was proved either two ways qualitative and quantitative that synthesis of cross-linked ligand was successfully completed.

4.2 Styrene Polymerization Using Solid Supported Ligand

4.2.1 Catalyst recycle without regeneration

Polymerization was performed with using styrene as the monomer and ethyl 2-bromopropionate (EBrP). Table 4.3 represents the results obtained from ATRP of styrene using the TEDETA modified beads for four times recycling and the result with unmodified beads. CuBr was successfully immobilized onto XL-1 in the first run as the color change occurred from slightly yellow to green during the reaction after 20 minutes.

Table 4.3 : ATRP of styrene using insoluble bead with[a] and without TEDETA.

Run	Total Catalyst Complex[b] (g)	$M_{n,GPC}$ (g/mol)	$M_{n,th}$ (g/mol)	Conversion (%)	PDI	$f_{initiator}$
1	0.6006	15210	2340	11.24	2.49	0.15
2	0.6162	13960	2790	13.38	2.19	0.20
3	0.6287	26500	1810	8.68	1.87	0.07
4	0.6335	41920	1620	7.80	2.15	0.04
Control[c]	0.5026	152770	930	4.47	1.61	0.006

a) [St]=7.27 mol/L, [EBrPr]=[CuBr]=[Ligand]= 0.036 mol/L for 2h at 110 ^{o}C in 2 mL of toluene. [St]:[EBrPr]:[CuBr]:[XL-1]= 200:1:1:1.

b) Total amount of solid ligand and CuBr.

c) Polymerization experiment without TEDETA (using X-PGMA-1).

CuBr catalyst (0.0626 g) was loaded onto XL-1 in the first run there was no addition of catalyst further runs (2, 3 and 4). Weight of total catalyst complex gradually increased upon recycling. This may be due to several reasons that the oxidation of Cu(I) to Cu(II) during the reaction process shown before (Figure 3.4), the catalyst complex might not got well dried and some polymer chains may be adsorbed into it.

In order to demonstrate TEDETA effect on ATRP of styrene using supported catalyst, control reaction was also performed using bead without TEDETA. The lowest conversion of styrene and initiator efficiency was monitored in control

reaction as seen on Table 4.3. That was expected result, because no color change on X-PGMA sample was observed during ATRP reaction.

To show the molecular weight trend upon recycling and compare if the reaction was done without unmodified beads, polymers were analyzed by GPC. Figure 4.2 shows GPC graph of styrene polymerization with XL-1 (4 runs) and with X-PGMA-1.

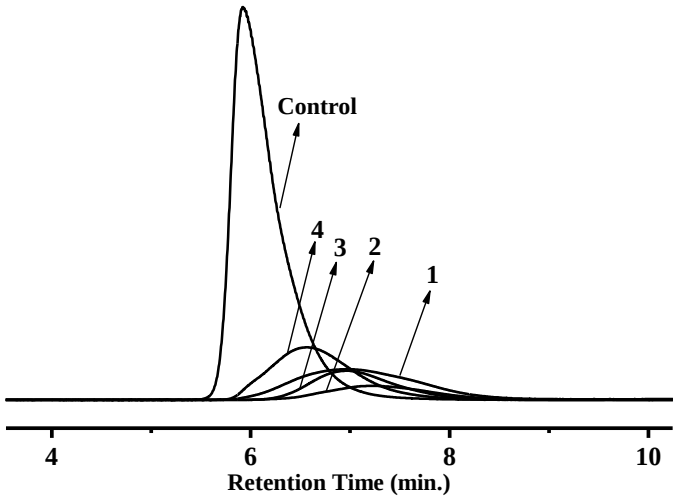

Figure 4.2 : GPC graph of different run circles and control run.

As the number of run circle increases, initiator efficiency increases in the second run then decreases gradually that shows the increasing molecular weight even if conversion decreases. That is because there may be occurred some degradations on catalyst complex and oxidation of Cu(I) as mentioned above. Nevertheless, polydispersity values were in the range 1.5-2.5 and quite higher than those in homogenous ATRP [97] and much more lower than those in heterogeneous medium performed with silica gel supported ligand [23]. As it is expected in the control reaction, the molecular weight is much more than those reactions performed with XL and even more than fourth run. That shows us the reactions with XL-1 was more controlled and had higher initiator efficiency than with X-PGMA-1. This may be another proof that incorporation of TEDETA onto X-PGMA-1 was succeeded. Finally, there is one thing leaping to the eye on the table that polystyrene synthesized

in control reaction has the lowest PDI value even though it was no controlled reaction.

4.2.2 Block copolymerization

The block copolymer of PS-*b*-PMMA was successfully prepared by reinitiation method using PS macro initiator containing Br active end groups synthesized via XL-3 ligand with ATRP. The aim of this reaction was whether the polystyrene synthesized after first run in catalyst recycle process has active Brom ending to initiate a new polymerization and shows living behavior or not. Figure 4.3 shows the molecular weight of the starting PS macro initiator and block copolymers with MMA using ligands PMDETA and XL. The M_n increased from 13960 to 24520 under reactions conditions with PMDETA and to 14800 with XL. The final polydispersities, which were respectively 1.83 and 2.12, showed lower values than the initial PDI value (2.19) of PS.

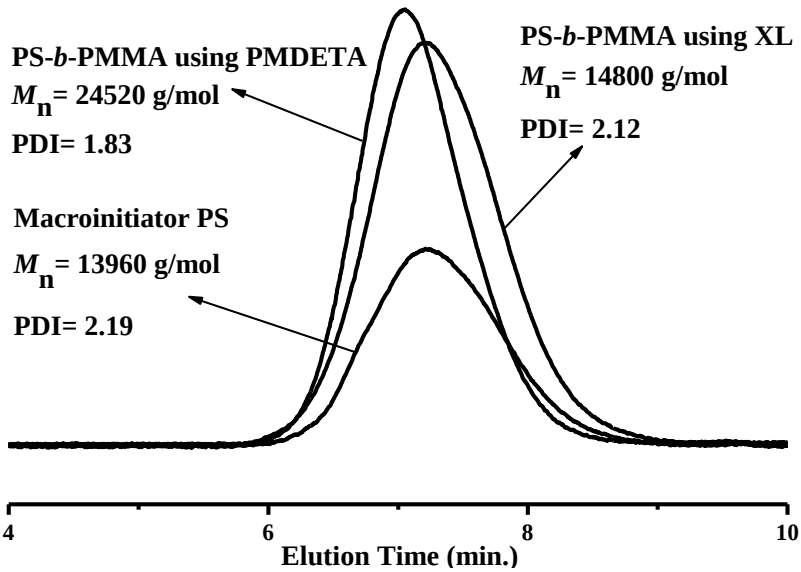

Figure 4.3 : GPC graph of (a) PS macro initiator, (b) PS-*b*-PMMA using PMDETA and (c) using XL-3.

According to NMR results shown in the following figures (Figure 4.4 and Figure 4.5), the peak due to two hydrogens of PMMA was seen at 3.60 ppm in NMR. It is clearly seen and expected that the cross-linked ligand XL-3 showed lower activity than soluble ligand PMDETA. That is, 66 units of MMA were bounded to PS chain via PMDETA. On the other hand, almost 2 units of MMA molecules were attached

to PS polymer with XL-3 at the same time. The reason may be that the reaction medium with XL-3 is heterogeneous and this causes the low rates compare to reaction in soluble catalyst/ligand system. In addition, it is difficult to form metal/ligand complex in heterogeneous ATRP because both ligand and catalyst are solid and it takes a long time to combine each other.

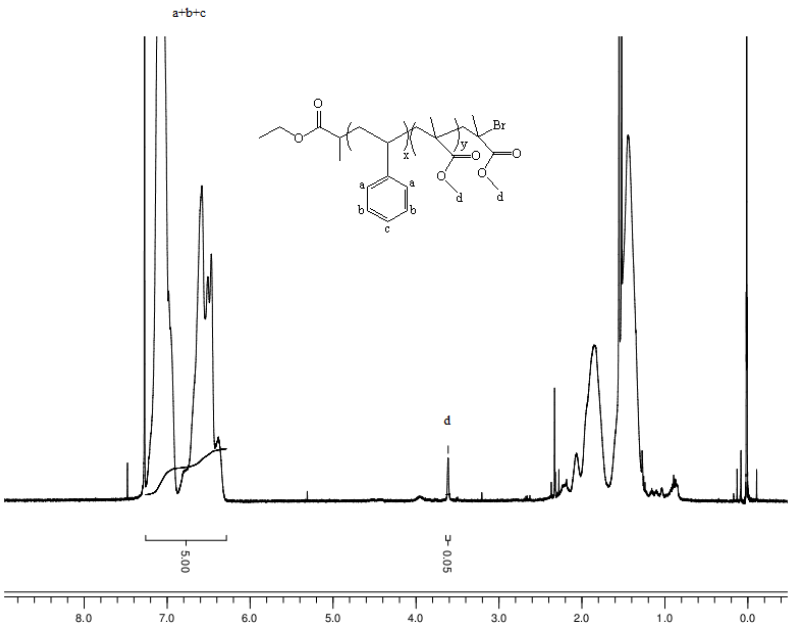

Figure 4.4 : ^{1}H NMR spectrum of PS-*b*-PMMA synthesized by using XL-3.

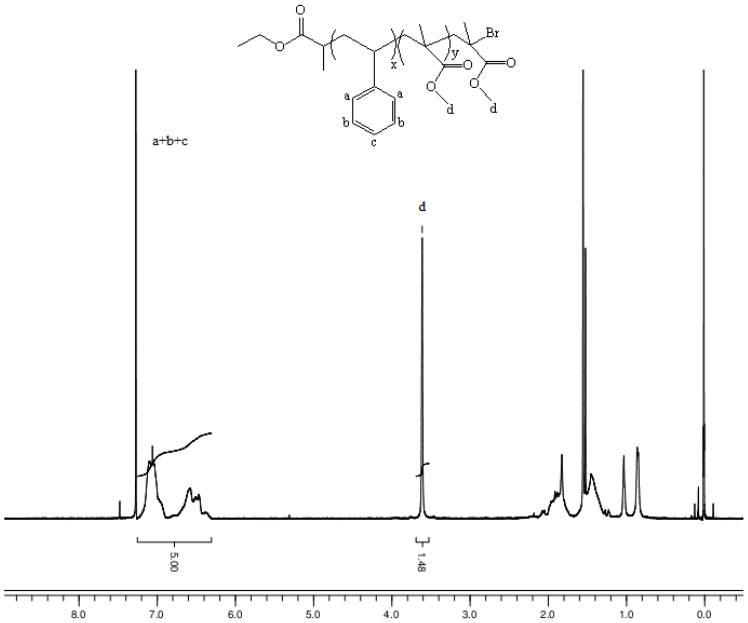

Figure 4.5 : ^{1}H NMR spectrum of PS-*b*-PMMA synthesized by using PMDETA.

4.3 Kinetic Studies of Styrene Polymerization Using Solid Supported Ligand

4.3.1 Catalyst recycle without regeneration

To monitor ATRP of styrene with fresh and recycled catalyst complexes, kinetic study was performed at the same conditions explained in Table 4.4.

Table 4.4 : ATRP of styrene using fresh and recycled catalyst complexes[a].

Run	k_p^{app} s^{-1}	Conversion[c] %	M_n[c] g/mol	$M_{n,th}$[c] g/mol	M_w/M_n[c]
First use[b]	3.7×10^{-5}	24	17400	5000	2.04
Second use[b]	1.5×10^{-5}	15	15010	3130	1.86
Third use[b]	1.2×10^{-5}	10	23180	2080	1.91

a) [St]= 7.27 mol/L, [EBrP]= 0.036 mol/L, [CuBr]=[XL-2]= 0.054 mol/L at 110 ^oC in 1 mL toluene. [St]:[EBrP]:[CuBr]:[XL-2]=200:1:1.5:1.5. b) First use: Run with fresh catalyst; Second use: Run with first recycled catalyst; Third use: Run with second recycled catalyst. c) Last sample on the polymerization.

In the first run, XL-2 beads were dispersed in polymerization solution by effective stirring. The slightly yellow colour of solid ligand turned to green with CuBr catalyst after 20 minutes. If the stirring was stopped, the green complex settled to the bottom of the flask and left a colorless upper layer. There was a bit amount of catalyst residue bottom of the flask, which was possibly not chelated by solid ligand. St polymerization with CuBr/XL-2 complex for first use was a typical first-order reaction with respect to monomer. After polymerization, some CuBr catalyst remained bottom of flask mentioned above and the colourless polymerization mixture was cooled down to room temperature, a few drops of methanol were added to this mixture so as to deactivate still active radicals. The solution was then diluted with DCM, was subsequently filtered to separate green CuBr/XL-2 complex and precipitated in methanol. The remaining catalyst complex was washed well with toluene and dried, which was then used for a second polymerization cycle where the same amounts fresh toluene, St and initiator as in the first run were charged to the flask. After that, catalyst complex was recycled for one more. There was an important point that polymer solution in second use had slightly green colour, furthermore, the colour tone increment was seen in the third one. This can be ascribed to releasing of catalyst from XL-2. Figure 4.6 shows that fresh and recycled

catalysts mediated a first-order polymerization showing induction period time 20, 20 and 28 minutes, respectively.

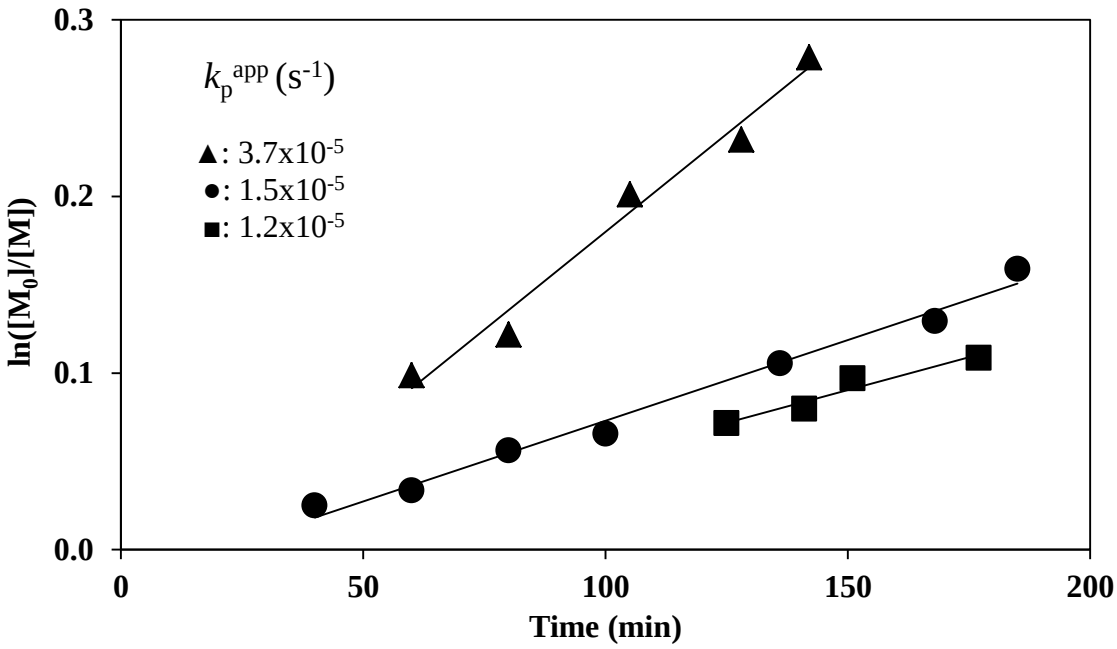

Figure 4.6 : Kinetic plots of styrene polymerization with fresh and recycled catalyst complexes without regeneration. ▲= first use; ●= second use; ■= third use. [St]= 7.27 mol/L, [EBrP]= 0.036 mol/L, [CuBr]=[XL-2]= 0.054 mol/L at 110 ^{o}C in 1 mL toluene. [St]:[EBrP]:[CuBr]:[XL-2]= 200:1:1.5:1.5.

The first and second recycled catalysts retained 40% and 32% to initial activity (k_p^{app} ratios), respectively. The activity reduction of the recycled catalysts was also observed in other supported catalyst systems for ATRP [23-25, 27-28, 98]. First, the reduced activity might be caused by loss of some supported catalysts when isolating polymer. In addition, there was some $CuBr_2$ produced in the first run. The presence of Cu(II) in the recycled catalyst may markedly decrease the polymerization rate even in the presence of a small amount of it [1, 25, 98-99]. Second, there could be some side reactions of the catalyst. That was partially true for CuBr/XL-2 system. It was seen in recycling processes that the colour of CuBr/XL-2 complex turned slightly brown at given reaction temperature but it had still a green type of colour (shaded). Molecular weights and polydispersities of three polymerization runs are shown in Table 4.3. As it seen that the molecular weights of polystyrene prepared by fresh and recycled catalysts were higher than theoretical values showing lower initiator efficiencies calculated 0.3, 0.2 and 0.1 for each run, respectively. And also, the polydispersities were close to 2, higher than those in soluble support system for

ATRP of MMA [29] and homogenous ATRP [97] and were mostly narrower than those from heterogeneous ATRP of styrene [23]. It can be resulted that the recycled catalyst did not have good molecular weight development as in the given literatures [29,97] with low initiator efficiencies. Nevertheless, molecular weight increment were better than those styrene polymerization [23]. These results indicate that the XL-2 supported CuBr could be recyclable.

4.3.2 Catalyst recycle with regeneration using reducing agent

In order to show how the polymerization reaction kinetics would have been affected, for example, if it would get improved, or not, p-methoxy phenol was used to reduce Cu(II) to Cu(I) to regenerate recycled catalysts. In previous study, a kind of regeneration of catalyst complex which was done with Cu metal out of the reactor and used after it had been successful to increase the activity [25].

All conditions with using XL-3 sample beads, as a ligand and observations were same for first run mentioned previous chapter. After polymerization, a bit amount of CuBr catalyst remained bottom of flask and the colourless polymerization mixture was cooled down to room temperature, a few drops of methanol were added to this mixture so as to deactivate still active radicals. Enough amount of DCM was added to the solution in order to dilute, the solution was subsequently filtered to separate green CuBr/XL-3 complex and precipitated in methanol. The remaining catalyst complex was washed well with toluene and dried, which was then weighted 0.4462 g and higher than the total charged amount of CuBr and XL-3, that was 0.4118 g. The weight difference, 0.0471 g, between first and last catalyst complex was assumed due to the oxidation of CuBr to $CuBr_2$. The corresponding mol amount of Br was calculated as much as that weight difference and the same amount of p-methoxy phenol (0.589 mmol) as a reducing agent (RA) which is soluble in toluene was taken to perform second run with that catalyst complex and the same amounts of fresh toluene, St and initiator as in the first run were charged to the flask. The polymerization mixture had a slightly green colour. After that, catalyst complex was recycled for one more doing the same regeneration process as after first polymerization. The last weight of complex 0.5146 g and the difference with the charged amount was 0.0684 g. 0.856 mmol p-methoxy phenol was charged to flask with that catalyst complex to perform third run using the same amounts of toluene, St

and initiator as in the first run. As distinct from second polymerization mixture, the colour got slightly green-brown. As shown in Figure 4.7, the regenerated recycled catalyst showed higher activity than the recycled catalyst without regeneration and lower activity than the fresh catalyst. The first and second recycled and regenerated catalysts retained 51% and 45% to initial activity (k_p^{app} ratios), respectively. These results demonstrated the presence of Cu(II) in the recycled catalyst. Fresh and regenerated catalyst complexes mediated a first order polymerization with respect to monomer showing induction period time 17, 0 and 22 minutes, respectively.

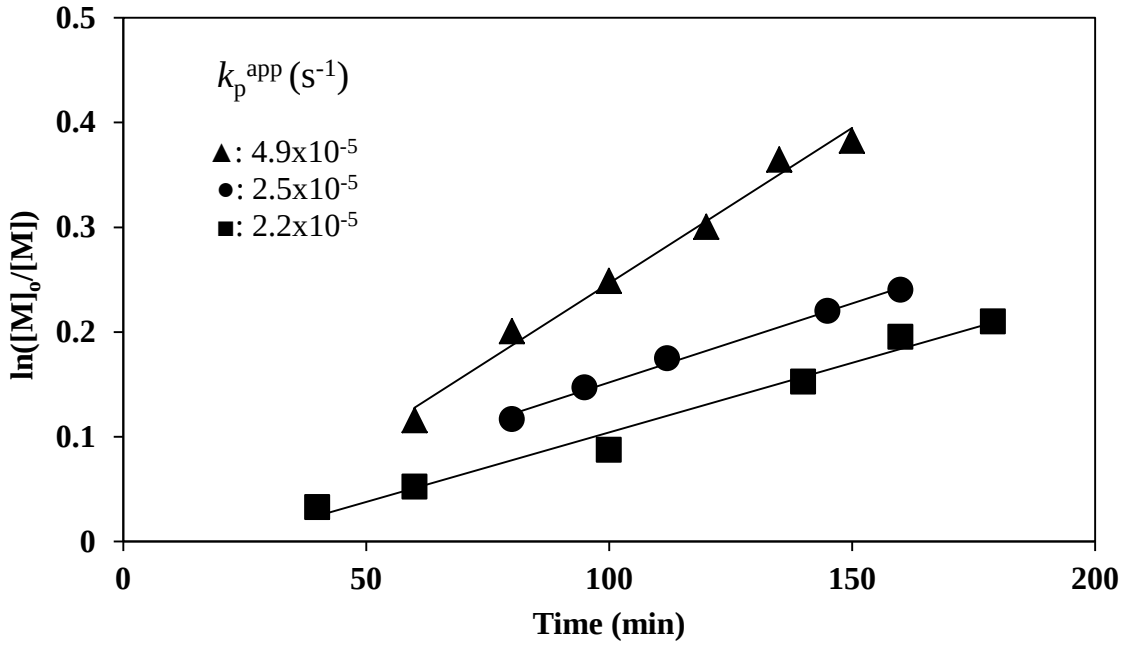

Figure 4.7 : Kinetic plots of styrene polymerization with fresh and recycled catalyst complexes by regeneration using reducing agent. ▲= first use; ●= second use with [RA]= 0.01 mol/L; ■= third use with [RA]= 0.14 mol/L. [St]= 7.27 mol/L, [EBrP]= 0.036 mol/L, [CuBr]=[XL-3]= 0.054 mol/L at 110 ^{o}C in 1 mL toluene. [St]:[EBrP]:[CuBr]:[XL-3]= 200:1:1.5:1.5.

For all kinetic samples, GPC measurements shown in Figure 4.8 were carried out to monitor molecular weight improvements. The molecular weights of PS from fresh and regenerated catalysts were not close to the predicted values, with high polydispersity values ($2.2 < M_w/M_n < 2.6$), typical of conventional free-radical polymerization, which may be explained by propagation being faster than initiation or by slow deactivation, and also may be because of the reaction between Cu(II) and excessive amount of reducing agent which was calculated depending on weight difference. The continuous reaction of Cu(II) with reducing agent during the

polymerization promoted the reactions. The molecular weight increased immediately and independently with the conversion in the initial times of polymerization and then grown slowly. This may be due to low initiator efficiency. These catalyst complexes again caused low initiator efficiencies compare with literature [29, 97], but better than these results observed before [23]. Additionally, complexes demonstrated controlled reaction in terms of molecular weights, which were increased linearly.

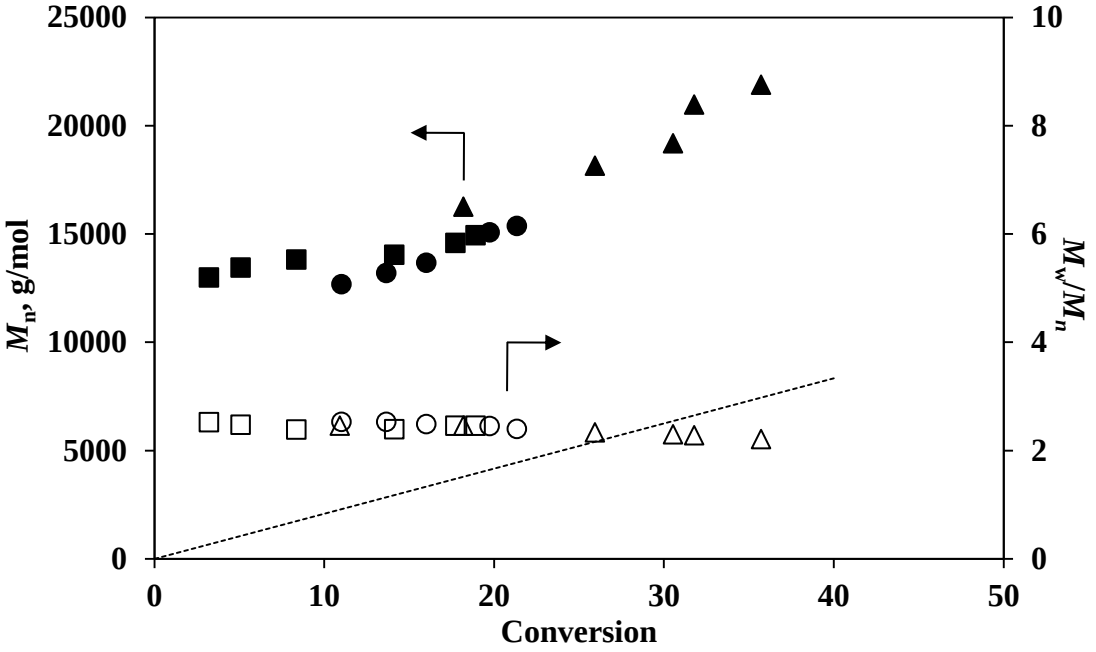

Figure 4.8 : Molecular weight versus conversion plots of styrene polymerization with fresh and recycled catalyst complexes by regeneration using reducing agent. ▲, Δ= first use; ●, ○= second use with [RA]= 0.01 mol/L; ■, □= third use with [RA]= 0.14 mol/L, theoretical M_n (---). [St]= 7.27 mol/L, [EBrP]= 0.036 mol/L, [CuBr]=[XL-3]= 0.054 mol/L at 110 ^oC in 1 mL toluene. [St]:[EBrP]:[CuBr]:[XL-3]= 200:1:1.5:1.5.

4.3.3 Catalyst recycle with regeneration using both reducing agent and fresh catalyst

Unlike previous section, additional fresh catalyst (CuBr) reinforcement was performed to regenerate the catalyst complex with reducing agent. The needed amount of p-methoxy phenol for second and third run was calculated as 0.047 g for second run and 0.1097 g for third run as in the previous chapter. There was a bit amount of CuBr, not being chelated with solid ligand, which still remained bottom of the flask after the reaction, where it had not been taken into account before. In this part, it was considered and fresh CuBr, which had the same amount of the remained amount in the flask, was charged to flask in the second and third run. Colours of

those runs were also changed to slightly green and then green-brown while the first run was colourless. Reaction conditions and the kinetic plot of the polymerization of styrene with recycled and regenerated catalysts using both reducing and fresh catalyst were given in Figure 4.9. It can be seen that the regenerated recycled catalysts showed higher activity than those previous studies done without regeneration and with regeneration using only reducing agent and lower activity than the fresh catalyst. The fresh and regenerated catalyst complex dramatically retained the same activity in spite of very small amount of CuBr used, later on a decrease on activity was observed in the second recycled and regenerated catalyst complex. It was still shown 74% to initial activity in the last run. It can be resulted CuBr reinforcement was showed well improvement on the activity of polymerization. These results also demonstrated the presence of Cu(II) in the recycled catalyst, otherwise that regeneration process would have made the activity higher than first one. Fresh and regenerated catalyst complexes mediated a first order polymerization with regard to monomer showing induction period time 17, 18 and 13 minutes, respectively.

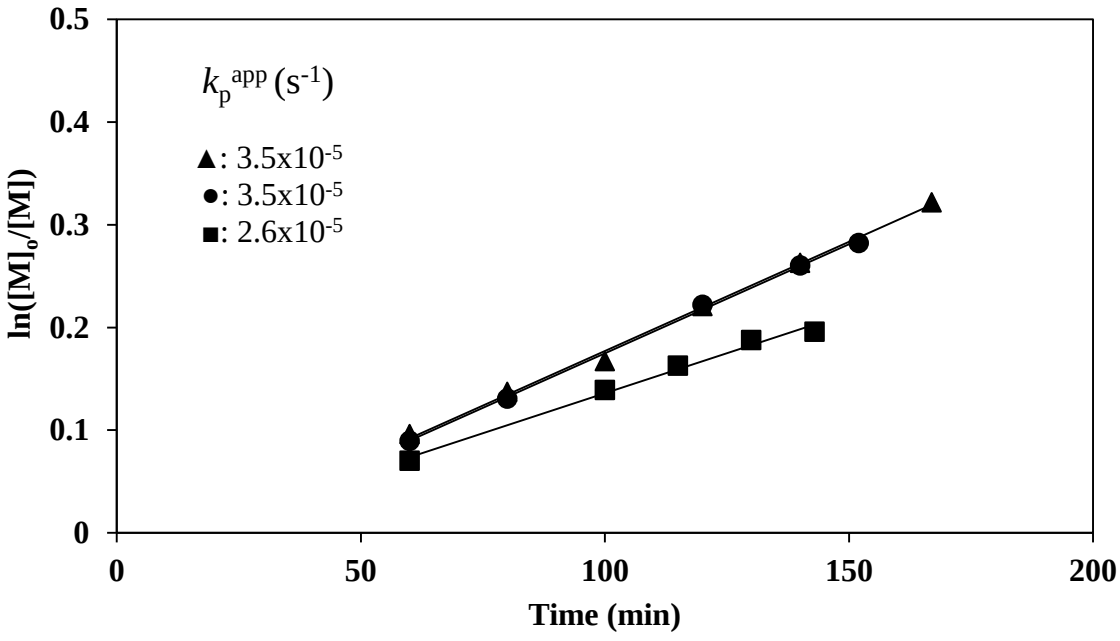

Figure 4.9 : Kinetic plots of styrene polymerization with fresh and recycled catalyst complexes by regeneration using reducing agent and CuBr. ▲, Δ= first use; ●, ○= second use with [RA]= 0.063 mol/L and [CuBr]= 0.007 mol/L; ■, □= third use with [RA]= 0.146 mol/L and [CuBr]= 0.007 mol/L. [St]= 7.27 mol/L, [EBrP]= 0.036 mol/L, [CuBr]=[XL-3]= 0.054 mol/L, [St]:[EBrP]:[CuBr]:[XL-3]= 200:1:1.5:1.5 at 110 ^{o}C in 1 mL toluene.

According to molecular weight analysis shown in Figure 4.10, the molecular weights of PS from fresh and regenerated catalysts were not close to the predicted values as previous experiments done with only reducing agent, with high polydispersity values ($1.9 < M_w/M_n < 2.5$) as in the typical of conventional free-radical polymerization, which may also be explained as in the previous section by propagation being faster than initiation or by slow deactivation, and also may be because of the reaction between Cu(II) and excessive amount of reducing agent. The continuous reaction of Cu(II) with reducing agent during the polymerization promoted the reactions. These catalyst complexes again showed low initiator efficiency over the polymerization compare with literature [29, 97], but it was better than these results observed before [23]. The molecular weights of PS obtained from those fresh and regenerated catalyst complexes increased linearly but also immediately and independently as in the previous studies with the conversion in the initial times of polymerization and then grown slowly. Nonetheless, it can be said that the polymerization was controlled by that catalyst complex.

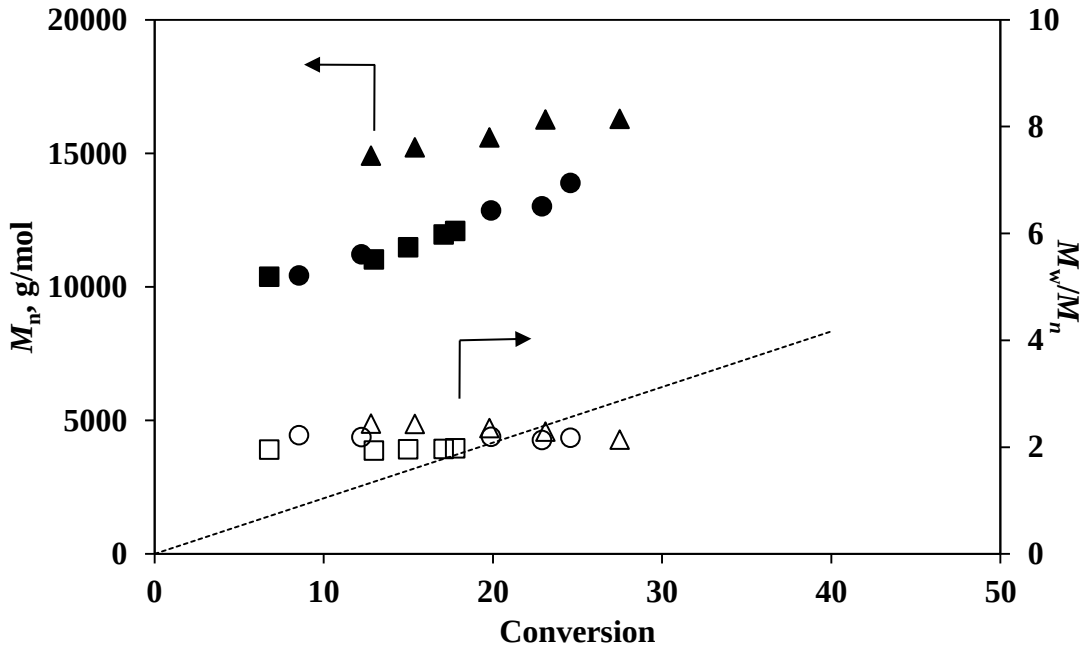

Figure 4.10 : Molecular weight versus conversion plots of styrene polymerization with fresh and recycled catalyst complexes by regeneration using reducing agent and fresh catalyst. ▲, Δ= first use; ●, ○= second use with [RA]= 0.063 mol/L and [CuBr]= 0.007 mol/L; ■, □= third use with [RA]= 0.146 mol/L and [CuBr]= 0.007 mol/L, theoretical M_n (---). [St]= 7.27 mol/L, [EBrP]= 0.036 mol/L, [CuBr]=[XL-3]= 0.054 mol/L, [St]:[EBrP]:[CuBr]:[XL-3]= 200:1:1.5:1.5 at 110 ^oC in 1 mL toluene.

5. CONCLUSION

In this study cross-linked poly(glycidyl methacrylate) beads produced by conventional free-radical suspension polymerization, which was chemically modified by TEDETA depending on epoxy ring opening reaction. The TEDETA ligand attached beads was used in ATRP of styrene with/without regeneration. The apparent rate of polymerizations was found to be first order in the monomer concentration. In all processes, with and without regeneration, the polymers roughly displayed polydispersities in the range of 1.8 and 2.5 and showed not too much molecular weights which were quite good results according to the literatures. These reactions showed that XL/CuBr insoluble ligand complex gave gradually decreasing activity and showed low initiator efficiencies compare to homogenous ATRP upon recycling might be the limited mobility of the supported catalyst and/or the steric hindrance and incompabilities between the immobilized catalyst and the polymer chain, therefore that causes less efficient halide atom transfer compared with homogenous ATRP. It might also be because of heterogeneous medium and oxidation of Cu(I) to Cu(II) or loss of catalyst. This problem was almost solved using additional fresh catalyst and reducing agent. The regeneration with only reducing agent and with both reducing agent and CuBr significantly improved activity of catalyst. The activity of catalyst complex had reduced after recycling done with/without reducing agent but was then regained by reaction with reducing agent and CuBr in the second use then decreased in third use. The block copolymerization with MMA was achieved onto PS synthesized by solid supported catalyst. It is demonstrated that the block copolymerization confirmed its living nature due to active Brom endings existed on resulted PS. Insoluble cross-linked beads without TEDETA showed very low activity on polymerization process contrast to those with TEDETA. All of these results showed that the new insoluble ligand could be recoverable, beside it could mostly solve the coloring problem of the obtained polymer.

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Y. Seki, K. Sever, M. Sarikanat, A. Sakarya and **E. Elik**. (2013). *Effect of huntite mineral on mechanical, thermal and morphological properties of polyester matrix*, Composites Part B: Engineering, *45*, 1534-1540.

PUBLICATIONS/PRESENTATIONS ON THE THESIS

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